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## Scale formation and prevention in the presence of hydrate inhibitors

M. B. Tomson, SPE, A. T. Kan, SPE, G. Fu, M. Al-Thubaiti, SPE, Rice University Brine Chemistry Consortium

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### Abstract

Hydrate formation can be a serious problem in many gas production systems. Large volumes of hydrate inhibitors (e.g., methanol, ethanol, ethylene glycol, and triethylene glycol as cosolvent) are often added to control hydrate formation. Such practice has an adverse effect on scale formation since the mineral salts are generally less soluble in the cosolvent. Due to production from reservoirs oilfield brines are often close to saturation as they enter a well, and even a small amount of added methanol, ethanol, etc., is often sufficient to induce various minerals to precipitate. The scaling tendency of sparingly soluble mineral salts, e.g., calcite and barite, in methanol/brine and ethanol/brine solutions is observed to be orders of magnitude larger than in the brine alone. Halite scaling is also severely affected in the presence of methanol or ethanol. Ethylene glycol and triethylene glycol have a lesser adverse effect on mineral salt scaling tendency. There is no accepted methodology to correlate the effects of hydrate inhibitors on scale formation as there is for electrolytes. Similarly, the effect of hydrate inhibitor on scale inhibition with common inhibitors is not well known. In this paper, a semi-empirical approach is proposed to correlate the effect of hydrate inhibitors on scale formation and inhibition from experimental solubility measurements of halite, barite, gypsum, calcite and carbonate equilibrium chemistry. The ion-cosolvent activity coefficients can be used directly in any solution speciation code to evaluate the effect of cosolvent on mineral scale formation. The validity of the equation has been tested between 4–50 °C and 1–6 M ionic strength. Working equations that can be used in gas and oil production to calculate the effect of cosolvents on scale formation will be presented. Such equations have been incorporated into ScaleSoftPitzer V.4.0. ScaleSoftPitzer™ is a Microsoft™ Excel™ based program to predict scale tendency, specifically written for the oil and gas production systems. Details of using ScaleSoftPitzer V.4.0 to predict hydrate inhibitor induced

scale formation and case studies will be presented. Initial tests of scale inhibitor efficiency in methanol will also be presented.

### Introduction

Methanol, ethylene glycol and triethylene glycol are industrial solvents and raw materials for a variety of processes. In the oil and gas industries, methanol, ethylene glycol and triethylene glycol are often used to inhibit gas hydrate formation during production. Gas hydrate is a crystalline solid consisting of gas molecule surrounded by a cage of water molecules, which forms at certain high pressure and low temperature regimes. Gas hydrate formation is particularly troublesome for offshore gas wells where the producing temperature is low due to both adiabatic expansion of gas and seawater cooling. Once gas hydrate forms, it can plug up the well and prevent gas production. One economic solution to prevent hydrate formation is to inject a large quantity of methanol, ethylene glycol or triethylene glycol. However, these hydrate inhibitors may cause adverse scaling problems in the associated brine solution, which often contains high concentrations of dissolved minerals.

In the following, the solubility of calcite, three sulfate salts and halite in these mixed solvent systems are discussed. Inhibition of barite scale formation by inhibitors is studied in these hydrate inhibitor/salt solutions. The impact of hydrate inhibitor on scaling under realistic oilfield condition is predicted by ScaleSoftPitzer™, a scale prediction software specifically written for the oil and gas industries.

### Observations

There is little research on the solubility of mineral salt in hydrate inhibitors/water/salt solutions. In an earlier paper by the authors<sup>1</sup>, the calcite solubility in methanol/water/salt solution was studied. In a second paper by the authors, a large number of halite, barite, celestite, and gypsum dissolution in hydrate inhibitors/water/salt solutions were reported<sup>2</sup>. Detail experimental procedures and results were discussed in these two papers.

The solubility studies has been tested over the range of 1–6 m ionic strength and 4 – 50 °C. Methanol significantly reduces the solubility of all mineral salts tested, i.e., halite, barite, calcite, celestite, and gypsum. For example, the effects of methanol on three sulfate mineral solubilities are illustrated in Figure 1. The solubility of each of the three sulfate minerals is reduced by more than one order of magnitude with about 0.35 mole fraction of methanol, which is equivalent to approximately 50% (wt) in methanol concentration. In addition to methanol, we have limited data on the effect of ethylene glycol and triethylene glycol on barite and halite

solubilities. There is a significant difference in the effect of ethylene glycol, triethylene glycol and methanol on barite and halite solubilities. Ethylene glycol and triethylene glycol reduce both barite and halite solubilities to a lesser extent than methanol (See Figure 2).

### Solution speciation model

A self-consistent set of activity coefficients for ions-electrolyte-cosolvent interactions was developed. First, it is assumed that, in each case,  $\gamma_{\text{overall}} = \gamma^S \cdot \gamma^N$ , where  $\gamma^S$  is the activity coefficient due to the salt effect and  $\gamma^N$  is the activity coefficient due to alcohol effect. For example, it is assumed that the activity coefficients of aqueous carbon dioxide,  $\gamma_{\text{CO}_2, \text{aq}}$ , can be written as a product of the effect of salt and of neutral methanol,  $\gamma_{\text{CO}_2, \text{aq}} = \gamma_{\text{CO}_2, \text{aq}}^S \cdot \gamma_{\text{CO}_2, \text{aq}}^N$ . The activity coefficient due to the salt effect,  $\gamma^S$ , is given by conventional method for activity coefficients, e.g., the Pitzer theory, with all concentration units as “aqueous molality” (moles of solute per kilogram of water).  $\gamma^N$ , the activity coefficient due to the cosolvent effect, is a curve fitted parameter obtained using an equation similar to the Born equation. The concentration of all aqueous species is expressed in units of aqueous molality (moles/kg of water). It is important to emphasize that all concentrations are expressed as moles of solute per kilogram of water, even in the presence of a substantial quantities of methanol; this is as required for conventional activity coefficient calculations, e.g., Pitzer theory, which uses ions in pure water as the reference state in all conditions. The approach is similar to that of Chen et al.<sup>3</sup>, where they combine Pitzer's extended Debye-Hückel equation for long range ion-ion interaction with the non-random two-liquid equation<sup>4</sup> for short range interactions and the Born equation for mixed solvent systems to convert reference conditions from infinite dilution in the mixed solvent system to infinite dilution in an aqueous solution<sup>5</sup>.

In Table 1 is listed the equations that illustrate the activity coefficient relationships. Numerical values of thermodynamic constants at 25 C and 1 atm are used for illustration. The activity of water in methanol water solution ( $a_{\text{H}_2\text{O}}^N$ ) is determined by the ratio of vapor pressure of water over the methanol/water mixture and over water. The term  $a_{\text{H}^+}^*$  refers to the activity of the hydrogen ion in the mixed solvent, which is corrected for medium effect in the mixed solvent via the  $\Delta\text{pH}_j$  and  $\delta$ -parameter<sup>1,6,7</sup>. In principle, the free energy of transfer from a solution of one dielectric constant to another dielectric constant can be calculated via the Born equation (Eq. 1)<sup>5,6,8,9</sup>. Kan et al.<sup>1</sup> proposed that the functional form of Eq. 2 can be used to correlate all  $\gamma^N$  values to cosolvent concentrations.

$$\Delta G(\text{J} \cdot \text{mol}^{-1}) = 2.303 \cdot R \cdot T \cdot \log(\gamma^N) = 6.95 \cdot 10^5 \cdot \frac{Z_i^2}{r} \left( \frac{1}{\epsilon_s} - \frac{1}{\epsilon_w} \right) \quad (\text{Born eq}) \quad (1)$$

For methanol,

$$\log(\gamma^N) = 6.95 \cdot 10^5 \cdot \frac{Z_i^2}{2.303 \cdot R \cdot T \cdot r} \cdot (0.0115 \cdot x_{\text{MeOH}} + 0.0068 \cdot x_{\text{MeOH}}^2) \quad (2)$$

The linear term in Eq. 2 represents the primary Born effect of dielectric constant,  $\epsilon_s$ , on the free energy of the ions relative to water. Experimentally, the first term represents the majority of the observed data up to about 0.3 mole fraction. At higher methanol concentration, it has been demonstrated that the experimental data often deviates from the predictions of the Born equation<sup>6,8,10</sup> (See Table 2 and discussion below).

### Model parameters

In Table 2 is listed the correlations of  $\gamma^N$  values with hydrate inhibitor concentrations, using the functional form of Eq. 2. In Table 2 also lists the standard deviation of the curve fitted parameters and correlation coefficients. The mean activity coefficients ( $\gamma_{\text{MA}}^{\text{N}\pm} \equiv \sqrt{\gamma_{\text{M}^+}^N \cdot \gamma_{\text{A}^-}^N}$ ) are reported for barite, celestite, gypsum and halite in this paper. The methanol effect activity coefficients ( $\gamma_{\text{MA}}^{\text{N}\pm}$ ) can be determined from the equations in Table 1 using the data in Kan et al.<sup>1,2</sup>, Pitzer activity coefficients, and temperature dependence of the thermodynamic equilibrium constants as used in ScaleSoftPitzer<sup>TM</sup>.

Generally, excellent correlations were observed between the experimental data and model equations, except for  $\gamma_{\text{HCO}_3^-}^N$

for methanol,  $\gamma_{\text{NaCl}}^{\text{N}\pm}$  for ethylene glycol, and  $\gamma_{\text{BaSO}_4}^{\text{N}\pm}$  for ethylene glycol. This is because both  $\gamma_{\text{HCO}_3^-}^N$  for methanol,  $\gamma_{\text{NaCl}}^{\text{N}\pm}$  for ethylene glycol, and  $\gamma_{\text{BaSO}_4}^{\text{N}\pm}$  for ethylene glycol and triethylene glycol are only slightly different from one (1.00), or the ion - glycol interaction are different from typical cosolvent. Clearly, additional data is needed on this issue and is presently being collected at Rice University.

Sen et al.<sup>11</sup> proposed that the radius in Born equation is the sum of reciprocals of the minimum distances of approach of the cation and the anion ( $1/r_+ + 1/r_-$ ). The hydrated proton and other cations are often assumed to have a radius of 3 to 5 Å. However, the anionic radius is less well known. The carboxylic ion radius is of the order of 1.2 Å<sup>8</sup>. Sen et al.<sup>11</sup> reported the anionic ion radius of thirteen carboxylates to be in the range of 0.9 - 1.7 Å. If this is the case, the sum of reciprocals of the minimum distances of approach for the cation and anion ( $1/r_+ + 1/r_-$ ) should be close to 1.0. Interestingly, the first term of Eq. 2 for the monovalent and divalent ions is evaluated to be equal to 1.4 and 5.6, respectively, by assuming an ion radius of 1 Å at 25 °C. The first methanol terms of the correlations in Table 2 are 1.4 for  $\gamma_{\text{Na}^+}^N$ , 0.8 for  $\gamma_{\text{HCO}_3^-}^N$ , 3.4 for  $\gamma_{\text{Ca}^{2+}}^N$ , 3.5 for  $\gamma_{\text{CO}_3^{2-}}^N$ , 4.3 for  $\gamma_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}}^{\text{N}\pm}$ , 5.0 for  $\gamma_{\text{SrSO}_4}^{\text{N}\pm}$ , and 6.9 for  $\gamma_{\text{BaSO}_4}^{\text{N}\pm}$  which are certainly quite reasonable comparing to the first-principle prediction via Born theory.

### Scale Prediction.

The solution supersaturation index can be calculated according to Eqs. 3-7.

$$SI^{\text{Calcite}} = \log \left\{ \frac{[Ca^{2+}] \cdot [HCO_3^-]^2 \cdot \gamma_{Ca^{2+}}^S \cdot \gamma_{HCO_3^-}^N \cdot \gamma_{HCO_3^-}^{S^2} \cdot \gamma_{HCO_3^-}^{N^2} \cdot K_2}{P_{CO_2} \cdot \gamma_{CO_2,g} \cdot K_H \cdot K_1 \cdot K_{sp}^{\text{Calcite}}} \right\} \quad (3)$$

$$SI^{\text{Barite}} = \log \left\{ \frac{[Ba^{2+}] \cdot [SO_4^{2-}] \cdot \gamma_{Ba^{2+}}^S \cdot \gamma_{SO_4^{2-}}^S \cdot \gamma_{BaSO_4}^{N^2}}{K_{sp}^{\text{Barite}}} \right\} \quad (4)$$

$$SI^{\text{Gypsum}} = \log \left\{ \frac{[Ca^{2+}] \cdot [SO_4^{2-}] \cdot \gamma_{Ca^{2+}}^S \cdot \gamma_{SO_4^{2-}}^S \cdot \gamma_{CaSO_4}^{N^2} \cdot a_{H_2O}^{S^2} \cdot a_{H_2O}^{N^2}}{K_{sp}^{\text{Gypsum}}} \right\} \quad (5)$$

$$SI^{\text{Celestite}} = \log \left\{ \frac{[Sr^{2+}] \cdot [SO_4^{2-}] \cdot \gamma_{Sr^{2+}}^S \cdot \gamma_{SO_4^{2-}}^S \cdot \gamma_{SrSO_4}^{N^2}}{K_{sp}^{\text{Celestite}}} \right\} \quad (6)$$

$$SI^{\text{Halite}} = \log \left\{ \frac{[Na^+] \cdot [Cl^-] \cdot \gamma_{Na^+}^S \cdot \gamma_{Cl^-}^S \cdot \gamma_{NaCl}^{N^2}}{K_{sp}^{\text{Halite}}} \right\} \quad (7)$$

It should be noted that Eq. 3 is independent of pH<sup>12</sup>. SI is expected to be equal to 0.00 at equilibrium. A positive SI indicates a supersaturated condition and a negative SI indicates an undersaturated condition. The model parameters for  $\gamma^N$  and  $\gamma_{MA}^{N\pm}$  are depicted in the nomogram of Figure 3. For example, to determine the  $\gamma^N$  values in 50 vol% methanol, first draw a horizontal line (H line) from the 50% mark on the lower Y axis to intercept the curved line 1, the vol% vs. mole fraction curve. Secondly, a vertical line (V line) can be drawn through the intercept of H line and line 1. The intercept of the V line and X-axis shows the corresponding mole fraction of methanol (0.31 in this case). The intercepts of V line through curved lines 2-7 yield the corresponding methanol concentration in wt% (44%), dielectric constant (58),  $\gamma^N$  and  $\gamma_{MA}^{N\pm}$  values, respectively. Combining  $\gamma^N$  and  $\gamma_{MA}^{N\pm}$  with common activity coefficient calculations, e.g., Pitzer theory, the saturation indices of calcite, barite, celestite, gypsum, and halite at a given methanol concentration can be calculated in Eqs. 3-7.

In the following discussion, SI calculations were done using ScaleSoftPitzer<sup>TM</sup>. The software automatically includes the equilibrium constants and activity coefficients in methanol listed in Table 1 and 2. Details of the program have been discussed in earlier papers by the authors<sup>13,14</sup>.

### Recommended procedure to use the activity model.

The following procedure is recommended to estimate the effect of hydrate inhibitors on mineral solubility at a specific temperature, ionic strength, and cosolvent concentration, using barite and the brine composition listed in Table 3, brine #1 as an example:

(1) Determine the thermodynamic equilibrium constant of a mineral salt at a specific temperature. The temperature dependence of thermodynamic constants is well established in the literature<sup>15,16</sup>. For example, Eq. 8 can be used to calculate the thermodynamic constant of barite<sup>15</sup>.

$$pK_{BaSO_4(S)} = -136.035 + \frac{7680.41}{T(^{\circ}K)} + 48.595 \times \log_{10}(T(^{\circ}K)) - (0.394 - 1.119 \cdot 10^{-4} \cdot T(^{\circ}C)) \times P(\text{atm}) / 500$$

$$pK_{BaSO_4(s)} = 9.97 \text{ @ } 77^{\circ}\text{F, 1 atm} \quad (8)$$

(2) Convert concentration unit to moles/Kg H<sub>2</sub>O. Solution phase measurements of concentration are generally made by taking a specific volume of sample, e.g., mg/L, which can easily be converted to molarity unit (moles/L). All thermodynamic data are based on unit of moles/Kg H<sub>2</sub>O. Some error may be introduced in high salinity brine if this unit difference is not taken into consideration. If density and TDS (total dissolved solid concentration, mg/L) are known, the mg/L or molarity unit can be easily converted to moles/Kg H<sub>2</sub>O basis. Often the density of the brine is not measured or reported. In ScaleSoftPitzer, a relationship between TDS and density has been established by curve fitting the density of NaCl vs. TDS:

$$\rho_{\text{brine}}(\text{g/ml}) = 0.9991 + 0.6358 \times 10^{-6} \text{ TDS (mg/l)} \quad r^2 = 0.9995 \quad (9)$$

This relation is used to convert the concentration unit of mg/L to moles/Kg H<sub>2</sub>O.

$$[Ba^{2+}](\text{moles/Kg H}_2\text{O}) = \frac{M_{Ba^{2+}}(\text{moles/L H}_2\text{O})}{(0.9991 + 0.6358 \cdot 10^{-6} \text{ TDS} - \text{TDS}/10^6)} \quad (9)$$

For brine #1 in Table 3, the  $[Ba^{2+}]$  and  $[SO_4^{2-}]$  are  $0.45 \cdot 10^{-3}$  and  $0.21 \cdot 10^{-3}$  moles/Kg H<sub>2</sub>O.

(3) Determine the ionic interaction activity coefficient with one of the activity coefficient equations, e.g., Debye-Hückel, Davies, or Pitzer equations. For brine#1 of Table 3,  $\gamma_{Ba^{2+}}^S = 0.14$  and  $\gamma_{SO_4^{2-}}^S = 0.068$ , calculated by ScaleSoftPitzer<sup>TM</sup>.

(4) Determine the methanol effect activity coefficient ( $\gamma^N$  or  $\gamma_{MA}^{N\pm}$ ) from the equations in Table 8 or from the nomogram in Figure 3. For brine #1 of Table 3,  $\gamma_{BaSO_4}^{N\pm} = 12.73$  at 77°F with 50% methanol (v/v).

(5) If the solution composition is known, the saturation index values can be calculated via Eqs. 3-7. For brine #1 of Table 3, the barite SI = 3.13 at 77°F, 1 atm pressure with 50% methanol (v/v).

(6) Lastly, the amount of mineral salt that could precipitate from a solution of known composition (initially containing, e.g.,  $[Ba^{2+}]_0$  and  $[SO_4^{2-}]_0$ ) can be calculated from the equations in Table 1. For example, Eq. 10 is used to calculate the amount of barite (ppt<sub>barite</sub> in unit of mol/Kg H<sub>2</sub>O) that could precipitate from a solution of known composition in hydrate inhibitor/water/salt solution:

$$\text{ppt}_{\text{Barite}} = \frac{[\text{Ba}^{2+}]_0 + [\text{SO}_4^{2-}]_0 - x}{2}, \quad \text{where}$$

$$x = \sqrt{\left([\text{Ba}^{2+}]_0 + [\text{SO}_4^{2-}]_0\right)^2 - 4 \left([\text{Ba}^{2+}]_0 [\text{SO}_4^{2-}]_0 - \frac{K_{\text{sp}}^{\text{Barite}}}{\gamma_{\text{Ba}^{2+}}^S \cdot \gamma_{\text{SO}_4^{2-}}^S \cdot \gamma_{\text{BaSO}_4}^{\text{N} \pm 2}}\right)}$$

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Note that if  $\text{ppt}_{\text{Barite}}$  is negative, this corresponds to dissolution. For brine#1 of Table 3, the amount of barite that precipitated is  $2.129 \cdot 10^{-4}$  moles/Kg  $\text{H}_2\text{O}$ , which is equivalent to 49 mg/L  $\text{BaSO}_4$  precipitation at 77°F, 1 atm pressure with 50% methanol (v/v)..

### Effect of hydrate inhibitors on barite scale nucleation and inhibition

It has been observed that barite nucleation rate is significantly affected by the addition of methanol. We have systematically measured the barite nucleation time at both a varied methanol concentrations (0 - 40% by wt.) and a varied barium and sulfate (at equal molal) concentrations from 0.5 -1.1 mmoles/Kg  $\text{H}_2\text{O}$ . The experiments were done by first mixing a barium containing solution and a sulfate containing solution. The onset of nucleation was monitored by a turbidity meter over time using a data logger<sup>11</sup>. The induction time is operationally defined as the time when the rapid increase in turbidity is observed. In Figure 4a is plotted the turbidity reading versus logarithmic reaction time in seconds for seven nucleation kinetic experiments where the only variable is the methanol concentrations. In this example, the barium solution contains 1 m NaCl, 0.09 m Ca, 1.50 mm Ba and 5 mm PIPES buffer at pH 6.4. The sulfate solution contains 1 m NaCl, 0.09 m Ca, 1.44 mm sulfate, and 5 mm PIPES buffer at pH 6.4. Methanol was added to both the cationic and anionic solution to a fixed concentration. An equal volume of these two solutions were then mixed and the turbidity of the solution was monitored. As shown in Figure 4a, barite induction time was affected by as little as 5% (by wt) of methanol and the induction time is shortened more at higher methanol concentrations.

It has been observed that barite nucleation time ( $t_{\text{ind}}^0$ , sec) is related to the supersaturating state of the solution (SI), temperature (°K) and methanol concentration by Eq. 11:

$$\log_{10}(t_{\text{ind}}^0, \text{sec}) = \left\{ -2.235 + \frac{[1087.2 - 0.297 \cdot T]^2}{T^2 \text{SI}_{\text{Brine}}} - 0.123 \frac{[1087.2 - 0.297 \cdot T]^3}{T^3 \text{SI}_{\text{Brine}}^2} \right\} - 13.68 \cdot x_{\text{MeOH}}$$

(11)

In Eq. 11, the first term represents the effect of ions and temperature on barite nucleation<sup>11</sup> and the second term is an empirical function to account for the effect of methanol on nucleation rate. Very good agreement ( $r = 0.97$ ) between the observed and calculated induction time ( $\log_{10}(t_{\text{ind}}^0)$ ) are observed (Figure 4b) for times from a few seconds to about 3 hours.

The inhibitory effect of a phosphonate scale inhibitor (BHPMP, Bis-hexamethylene triamine-penta(methylene

phosphonic) acid) on barite nucleation has been studied at 0-40% methanol, ethylene glycol or triethylene glycol and 1.1 to 1.8 mm barium and sulfate concentrations. BHPMP is one of the most effective barite inhibitors<sup>17</sup>. In Figure 5 is plotted a typical set of nucleation studies where barium and sulfate concentrations are 1.1 mm (SI=2.0). The solutions also contain 1 m NaCl, 0.09 m Ca, 5 mm PIPES buffer (pH 6.4) and various concentrations of BHPMP and methanol or ethylene glycol. The four plots in Figure 5 are grouped by different methanol or ethylene glycol concentrations. In each plot of Figure 5, multiple nucleation data are plotted. These nucleation experiments were done at identical solution compositions, except for BHPMP concentrations. Increasing concentrations of BHPMP were added to successive experiments until a BHPMP concentration capable of inhibiting barite precipitation up to ~24 hours ( $\log t = 4.94$ ) was observed. As shown in Figure 5a, only 0.33 mg/L BHPMP was needed to inhibit the barite nucleation for 24 hours when no methanol was present. However, more BHPMP was needed at higher methanol concentrations. For example, 1.90 mg/L BHPMP were needed to inhibit barite nucleation in 20% methanol. Even though only 2.52 mg/L BHPMP was needed to inhibit barite precipitation in 30% methanol, low turbidity was observed at 3-5.3 mg/L BHPMP for the same solution (data not shown). The reason for the deteriorating inhibition effect at higher BHPMP concentrations is probably caused by the precipitation of Ca-BHPMP at higher methanol concentrations. The solubility of BHPMP in a similar sulfate free solution is measured to be ~2.0 mg/L in 30% methanol concentration and ~1.2 mg/L in 40% methanol concentration. If the phosphonate inhibitor solubility in methanol solution is limited, there should be a limiting methanol concentration that no phosphonate inhibitor will work. As shown in Figure 5c, no inhibitory effect was observed for BHPMP up to 5.8 mg/L concentration at 40% methanol. Interestingly, only 0.38 mg/L BHPMP is needed to inhibit barite precipitation from a similar solution containing 40% ethylene glycol (Figure 5d).

Similar comparison are made among ethylene glycol and triethylene glycol at 40% (w/w) concentrations and plotted in Figure 6. The brine contains higher barium and sulfate concentration than that used in Figure 5 (1.8 mm Ba and  $\text{SO}_4$  and SI=2.5 in the absence of the glycols). Approximately 2 mg/L BHPMP is needed to inhibit the brine in the absence of glycols. Similar inhibitor concentrations are needed to inhibit the barite precipitation in the presence of either ethylene glycol or triethylene glycol. These results are consistent with the solubility data, indicating a significant advantage in using ethylene glycol or triethylene glycol to control hydrate formation.

### Implication of hydrate inhibitor on barite, halite and calcite scale formation

In order to evaluate the impact of hydrate inhibitors to scale formation under realistic field conditions. Several typical brine and well conditions (Table 3) are selected to evaluate the impact of these hydrate inhibitors on barite, calcite and halite scaling tendency, mass of scale formation and inhibitor needs using ScaleSoftPitzer program. In Table 3, brine #1 has the composition of brine from a offshore gulf coast well and is used to illustrate the barite scaling problem. Brine #2 is a high TDS formation brine of Smackover field, Ar<sup>18</sup> and is used to

illustrate the halite scaling problem. Brine #3 and #4 are data from two Texas wells and are used to illustrate the calcite scaling problems. Brine #3 contains high Ca, low alkalinity, and low CO<sub>2</sub>, while brine #4 contains high alkalinity and high CO<sub>2</sub>. In Table 3 is also listed the actual well condition, temperature, pressure, production volume. The illustration is made to demonstrate the impact of 0-40% v/v addition of methanol on scale formation. The wellhead temperature was set at 4 °C for illustration purpose.

In Figure 7 is plotted the predicted amount of scale formation and saturation index values of barite versus the hydrate inhibitor concentration (% vol) under realistic oil field conditions. The simulation shows that considerable barite scale will form in the presence of as little as 5-20% methanol (by volume), much less impact is observed with ethylene glycol and triethylene glycol. Also shown on the graph is the estimated inhibitor concentration needed to control barite scale. In the absence of hydrate inhibitor, probably no inhibitor is needed, while very high concentration of scale inhibitor may be needed when high concentrations of methanol are added.

The effect of the three hydrate inhibitors on halite scale formation can be evaluated from Figure 8. In the absence of methanol, NaCl is soluble in water up to 6.1 m or approximately 318,000 mg/L TDS. Therefore, brine #2 should not have any halite scale problem when no hydrate inhibitor is added. However, the system may experience serious halite problems at 20+% methanol. The same well will remain undersaturated with up to 40% of either ethylene glycol or triethylene glycol.

In Figure 9 is plotted the effect of methanol on calcite scaling tendency. Wells that produce calcite scales may contain high Ca, high alkalinity or similar Ca and bicarbonate concentrations in the brine. Methanol is a better solvent for CO<sub>2</sub> gas than salt water. How methanol affects calcite scaling tendency is less intuitive. In Figure 9, we compare the calcite SI of two wells, one with a high Ca, low CO<sub>2</sub> brine and the other with a high alkalinity, high CO<sub>2</sub> brine. As expected, methanol has a slightly lesser effect on the well with high alkalinity brine than the well with high Ca brine.

In summary, a self-consistent activity model has been proposed to model the solubility of mineral salts in hydrate inhibitors/water/salt solutions. The model uses a procedure, similar to Born equation, to convert reference conditions from infinite dilution in the mixed solvent system to infinite dilution in an aqueous solution. The model has been validated up to 90 wt% and 0-25 °C for NaCl in methanol, 50 wt% and 0-50 °C for barite, 50 wt% and 0-25 °C for celestite, 50 wt% and 0-25 °C for gypsum. It should be emphasized that the validity of equations for  $\gamma_{\text{SrSO}_4}^{\text{N}^\pm}$ ,  $\gamma_{\text{BaSO}_4}^{\text{N}^\pm}$  and  $\gamma_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}}^{\text{N}^\pm}$  should be restricted to the range of the experimental data, which is approximately 0-0.36 mole fraction methanol (or 0 - ~50% by weight). These equations provide a predictive algorithm to assess the potentially adverse effect of methanol and ethylene glycol on mineral scale formation during oil and gas production.

## Conclusion

A new activity model (ScaleSoftPitzer™) is proposed to model the methanol effect on mineral salt scaling tendency in oil and gas production system. The model uses Pitzer theory to

model the effect of salt and Born equation to model the effect of methanol. The model predicts potentially significant barite and calcite scaling problems with as little as 5% to 20% methanol in a well. Halite scale problem can occur at >210,000 mg/L TDS when 50% (vol.) methanol is present in the production system. Barite nucleation rate is accelerated in as little as 5% methanol. A semiempirical equation has been developed to predict the kinetics of barite scale formation as a function of methanol concentration. More scale inhibitors are needed to inhibit barite scale when methanol is added to the production system. Barite scale control may become impossible when substantial amount of methanol are used for hydrate control. Ethylene glycol has less adverse effects than methanol in both scale formation and inhibition.

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## Nomenclature

$A$	= an anion
$a_{\text{H}^+}^*$	= the hydrogen ion activity in the mixed solvent
$a_{\text{H}_2\text{O}}$	= the activity coefficient of water
$a_{\text{H}_2\text{O}}^S$	= the activity coefficient of water due to the salt
$\text{effect}$	
$a_{\text{H}_2\text{O}}^N$	= the activity coefficient of water due to the alcohol effect
$a_M$ and $a_A$	= the activities of a cation and anion
$a_q$	= the aqueous phase species
$e$	= the elementary charge ( $=1.6 \times 10^{-19}$ coulomb)
$g$	= the gas phase species
$I$	= the ionic strength (moles/Kg H <sub>2</sub> O)
$K_{\text{sp}}^{\text{MA}}$	= the solubility product of a mineral salt
$K_H$	= the Henry's law constant (mole/Kg H <sub>2</sub> O-atm)
$K_1$ and $K_2$	= the first and second dissociation constants of carbonic acid
$M$	= a cation
$[]$	= concentrations in moles/Kg H <sub>2</sub> O
$N$	= the Avogadro constant ( $= 6.02 \times 10^{23} \text{ mol}^{-1}$ )
$\text{pH}_{\text{meter reading}}$	= the <u>observed</u> pH-meter reading in the mixed solvent when the pH electrode has been calibrated using normal aqueous buffers.
$\Delta \text{pH}_j$	= the correction term to represent the changes in electrode response due to the presence of salt. $\Delta \text{pH}_j$ can be estimated from the following eq. $\Delta \text{pH}_j = 0.129 \cdot I^{0.5} \quad r = 0.99$
$r$	= the ion radius (Å)
$SI$	= the saturation indices of mineral salt
$SI_{\text{Brine}}$	= the barite SI of the brine in the absence of methanol
$T$	= temperature (°K)
$t_{\text{ind}}$	= the barite induction time (sec)
$x_{\text{MeOH}}$	= mole fraction concentration of methanol in methanol-water mixture

- $x_{EG}$  = mole fraction concentration of ethylene glycol in ethylene glycol-water mixture
- $x_{EtOH}$  = mole fraction concentration of ethanol in ethanol-water mixture
- $z_i$  = the ion charge
- $\delta$  = the correction term used to represent the changes in electrode response due to methanol.  $\delta$  can be estimated from the following eq.

$$\delta = x_{MeOH}^2 \cdot \left\{ -0.0897 \cdot \exp(3.262 \cdot x_{MeOH}^2) + 1.309 \cdot \exp(-4.008 \cdot x_{MeOH}^3) \right\} \\ r = 1.00$$

- $\epsilon_0$  = the vacuum permittivity ( $= 8.854 \times 10^{-12} J^{-1} \cdot C^2 \cdot m^{-1}$ )
- $\epsilon_s$  = the dimensionless dielectric constant of the mixed solvent
- $\epsilon_w$  = the dimensionless dielectric constant of water
- $\gamma^S$  = the activity coefficient due to the salt effect
- $\gamma^N$  = the activity coefficient due to alcohol effect
- $\gamma_M^S$  and  $\gamma_A^S$  = the activity coefficient of a cation or anion due to the salt effect
- $\gamma_M^N$  and  $\gamma_A^N$  = the activity coefficient of a cation or anion due to the cosolvent effect
- $\gamma^{N\pm}$  = the mean activity coefficient due to cosolvent effect

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Table 1. Equilibrium parameters tested in methanol/water/salt solution; values are at 25 °C and 1 atm with ions in pure water as a reference state.

$$\begin{aligned}
K_H &= 10^{-1.47} \frac{\text{molal}}{\text{atm}} = \frac{a_{\text{CO}_2, \text{aq}}}{f_{\text{CO}_2, \text{g}}} = \frac{[\text{CO}_{2, \text{aq}}] \cdot \gamma_{\text{CO}_2, \text{aq}}}{P_{\text{CO}_2, \text{g}} \cdot \gamma_{\text{CO}_2, \text{g}}} = \frac{[\text{CO}_{2, \text{aq}}] \cdot \gamma_{\text{CO}_2, \text{g}}^S \cdot \gamma_{\text{CO}_2}^N}{P_{\text{CO}_2, \text{g}} \cdot \gamma_{\text{CO}_2, \text{g}}} \\
K_1 &= 10^{-6.35} = \frac{a_{\text{H}^+}^* \cdot a_{\text{HCO}_3^-}}{a_{\text{CO}_2, \text{aq}}} = \frac{10^{-(\text{pH}_{\text{meter reading}} + \Delta\text{pH}_j - \delta)} \cdot [\text{HCO}_3^-] \cdot \gamma_{\text{HCO}_3^-}}{[\text{CO}_{2, \text{aq}}] \cdot \gamma_{\text{CO}_2, \text{aq}}} = \frac{10^{-(\text{pH}_{\text{meter reading}} + \Delta\text{pH}_j - \delta)} \cdot [\text{HCO}_3^-] \cdot \gamma_{\text{HCO}_3^-}^S \cdot \gamma_{\text{HCO}_3^-}^N}{[\text{CO}_{2, \text{aq}}] \cdot \gamma_{\text{CO}_2, \text{aq}}^S \cdot \gamma_{\text{CO}_2, \text{aq}}^N} \\
K_2 &= 10^{-10.33} = \frac{a_{\text{H}^+}^* \cdot a_{\text{CO}_3^{2-}}}{a_{\text{HCO}_3^-}} = \frac{10^{-(\text{pH}_{\text{meter reading}} + \Delta\text{pH}_j - \delta)} \cdot [\text{CO}_3^{2-}] \cdot \gamma_{\text{CO}_3^{2-}}}{[\text{HCO}_3^-] \cdot \gamma_{\text{HCO}_3^-}} = \frac{10^{-(\text{pH}_{\text{meter reading}} + \Delta\text{pH}_j - \delta)} \cdot [\text{CO}_3^{2-}] \cdot \gamma_{\text{CO}_3^{2-}}^S \cdot \gamma_{\text{CO}_3^{2-}}^N}{[\text{HCO}_3^-] \cdot \gamma_{\text{HCO}_3^-}^S \cdot \gamma_{\text{HCO}_3^-}^N} \\
K_{\text{sp}}^{\text{calcite}} &= 10^{-8.36} = a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_3^{2-}} = [\text{Ca}^{2+}] \cdot \gamma_{\text{Ca}^{2+}} \cdot [\text{CO}_3^{2-}] \cdot \gamma_{\text{CO}_3^{2-}} = [\text{Ca}^{2+}] \cdot \gamma_{\text{Ca}^{2+}}^S \cdot \gamma_{\text{Ca}^{2+}}^N \cdot [\text{CO}_3^{2-}] \cdot \gamma_{\text{CO}_3^{2-}}^S \cdot \gamma_{\text{CO}_3^{2-}}^N \\
K_{\text{sp}}^{\text{barite}} &= 10^{-9.69} = a_{\text{Ba}^{2+}} \cdot a_{\text{SO}_4^{2-}} = [\text{Ba}^{2+}] \cdot \gamma_{\text{Ba}^{2+}} \cdot [\text{SO}_4^{2-}] \cdot \gamma_{\text{SO}_4^{2-}} = [\text{Ba}^{2+}] \cdot \gamma_{\text{Ba}^{2+}}^S \cdot \gamma_{\text{Ba}^{2+}}^N \cdot [\text{SO}_4^{2-}] \cdot \gamma_{\text{SO}_4^{2-}}^S \cdot \gamma_{\text{SO}_4^{2-}}^N \\
&= [\text{Ba}^{2+}] \cdot \gamma_{\text{Ba}^{2+}}^S \cdot [\text{SO}_4^{2-}] \cdot \gamma_{\text{SO}_4^{2-}}^S \cdot (\gamma_{\text{BaSO}_4}^{\text{N}\pm})^2 \\
K_{\text{sp}}^{\text{celestite}} &= 10^{-6.47} = a_{\text{Sr}^{2+}} \cdot a_{\text{SO}_4^{2-}} = [\text{Sr}^{2+}] \cdot \gamma_{\text{Sr}^{2+}} \cdot [\text{SO}_4^{2-}] \cdot \gamma_{\text{SO}_4^{2-}} = [\text{Sr}^{2+}] \cdot \gamma_{\text{Sr}^{2+}}^S \cdot \gamma_{\text{Sr}^{2+}}^N \cdot [\text{SO}_4^{2-}] \cdot \gamma_{\text{SO}_4^{2-}}^S \cdot \gamma_{\text{SO}_4^{2-}}^N \\
&= [\text{Sr}^{2+}] \cdot \gamma_{\text{Sr}^{2+}}^S \cdot [\text{SO}_4^{2-}] \cdot \gamma_{\text{SO}_4^{2-}}^S \cdot (\gamma_{\text{SrSO}_4}^{\text{N}\pm})^2 \\
K_{\text{sp}}^{\text{gypsum}} &= 10^{-4.63} = a_{\text{Ca}^{2+}} \cdot a_{\text{SO}_4^{2-}} \cdot a_{\text{H}_2\text{O}}^2 = [\text{Ca}^{2+}] \cdot \gamma_{\text{Ca}^{2+}} \cdot [\text{SO}_4^{2-}] \cdot \gamma_{\text{SO}_4^{2-}} \cdot a_{\text{H}_2\text{O}}^2 \\
&= [\text{Ca}^{2+}] \cdot \gamma_{\text{Ca}^{2+}}^S \cdot [\text{SO}_4^{2-}] \cdot \gamma_{\text{SO}_4^{2-}}^S \cdot (\gamma_{\text{CaSO}_4}^{\text{N}\pm})^2 \cdot (a_{\text{H}_2\text{O}}^S \cdot a_{\text{H}_2\text{O}}^N)^2 \\
K_{\text{sp}}^{\text{halite}} &= 10^{1.59} = a_{\text{Na}^+} \cdot a_{\text{Cl}^-} = [\text{Na}^+] \cdot \gamma_{\text{Na}^+} \cdot [\text{Cl}^-] \cdot \gamma_{\text{Cl}^-} = [\text{Na}^+] \cdot \gamma_{\text{Na}^+}^S \cdot \gamma_{\text{Na}^+}^N \cdot [\text{Cl}^-] \cdot \gamma_{\text{Cl}^-}^S \cdot \gamma_{\text{Cl}^-}^N \\
&= [\text{Na}^+] \cdot \gamma_{\text{Na}^+}^S \cdot [\text{Cl}^-] \cdot \gamma_{\text{Cl}^-}^S \cdot (\gamma_{\text{NaCl}}^{\text{N}\pm})^2
\end{aligned}$$

Table 2. The correlation of activity due to methanol effect ( $\gamma^N$  and  $\gamma^{N\pm}$ ) with methanol concentrations (mole fraction), ionic strength and temperature.

$$\log(\gamma_{\text{CO}_2, \text{aq}}^N) = (-6.029 + 1444.9/T(^{\circ}\text{K})) \cdot x_{\text{MeOH}} - 1.170 \cdot x_{\text{MeOH}}^2 \quad r = 1.00$$

Standard deviations for the three parameters are 0.612, 175.4, and 0.135, respectively.

$$\log(\gamma_{\text{HCO}_3^-}^N) = (-3.338 + 955.9/T(^{\circ}\text{K})) \cdot x_{\text{MeOH}} + 0.565 \cdot x_{\text{MeOH}}^2 \quad r = 0.85$$

Standard deviations for the three parameters are 0.929, 260.8, and 0.211, respectively.

$$\log(\gamma_{\text{CO}_3^{2-}}^N) = (-1.957 + 1580.9/T(^{\circ}\text{K})) \cdot x_{\text{MeOH}} - 1.601 \cdot x_{\text{MeOH}}^2 \quad r = 0.99$$

Standard deviations for the three parameters are 0.520, 150.9, and 0.097, respectively

$$\log(\gamma_{\text{Ca}^{2+}}^N) = (19.343 - 4714.2/T(^{\circ}\text{K}) - 0.333 \cdot I) \cdot x_{\text{MeOH}} - 2.519 \cdot x_{\text{MeOH}}^2 \quad r = 0.97$$

Standard deviations for the four parameters are 0.861, 247.2, 0.0316 and 0.189, respectively

$$\log(\gamma_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}}^{N\pm}) = (4.706 - 0.423 \cdot I) \cdot x_{\text{MeOH}} - 4.153 \cdot x_{\text{MeOH}}^2 \quad r = 0.97$$

Standard deviations for the three parameters are 0.314, 0.092, and 1.205, respectively

$$\log(\gamma_{\text{SrSO}_4}^{N\pm}) = (4.963 - 0.206 \cdot I) \cdot x_{\text{MeOH}} - 4.017 \cdot x_{\text{MeOH}}^2 \quad r = 1.00$$

Standard deviations for the three parameters are 0.221, 0.0484, and 0.613, respectively

$$\log(\gamma_{\text{BaSO}_4}^{N\pm}) = (3.022 + 1167.6/T(^{\circ}\text{K})) \cdot x_{\text{MeOH}} - 10.89 \cdot x_{\text{MeOH}}^2 \quad r = 0.99$$

Standard deviations for the three parameters are 2.507, 723.2, and 1.046, respectively

$$\log(\gamma_{\text{BaSO}_4}^{N\pm}) = 2.590 \cdot x_{\text{EG}} - 5.316 \cdot x_{\text{EG}}^2 \quad r = 0.52$$

Standard deviations for the two parameters are 0.623 and 1.684, respectively

$$\log(\gamma_{\text{BaSO}_4}^{N\pm}) = 2.997 \cdot x_{\text{TEG}} - 5.774 \cdot x_{\text{TEG}}^2 \quad r = 0.84$$

Standard deviations for the two parameters are 0.626 and 1.313, respectively

$$\log(\gamma_{\text{NaCl}}^{N\pm}) = 1.385 \cdot x_{\text{MeOH}} - 1.104 \cdot x_{\text{MeOH}}^2 \quad r = 0.96$$

Standard deviations for the two parameters are 0.070 and 0.110, respectively

$$\log(\gamma_{\text{NaCl}}^{N\pm}) = 1.366 \cdot x_{\text{EtOH}} \quad r = 0.99$$

Standard deviations for the parameter is 0.018.

$$\log(\gamma_{\text{NaCl}}^{N\pm}) = 0.232 \cdot x_{\text{EG}} \quad r = 0.90$$

Standard deviations for the parameter is 0.038.

$$\log(\gamma_{\text{NaCl}}^{N\pm}) = 1.227 \cdot x_{\text{TEG}} - 4.181 \cdot x_{\text{TEG}}^2 \quad r = 0.99$$

Standard deviations for the parameter are 0.125 and 0.260, respectively.



**Table 3. Brine composition and well condition used to simulate methanol effect on scaling<sup>1</sup>.**

Brine #		1	2	3	4
Parameters	Units	Input	Input	Input	Input
Location		Offshore Gulf Coast	Arkansas	Texas, high Ca	Texas, high alkalinity
Na <sup>+</sup>	(mg/l)*	25,100	63,300	19,872	22,790
K <sup>+</sup> (if not known =0)	(mg/l)	0.00	1,370.00	500.00	1,145.00
Mg <sup>2+</sup>	(mg/l)	137.00	4,040.00	54.00	1,285.00
Ca <sup>2+</sup>	(mg/l)	1,230.00	36,300.00	6,500.00	6,820.00
Sr <sup>2+</sup>	(mg/l)	0.00	0.00	700.00	200.00
Ba <sup>2+</sup>	(mg/l)	60.00	0.00	550.00	0.90
Fe <sup>2+</sup>	(mg/l)	7.00	0.00	12.00	0.50
Zn <sup>2+</sup>	(mg/l)	0.00	0.00	10.00	0.00
Cl <sup>-</sup>	(mg/l)	41,000	197,600	43,000	50,980
SO <sub>4</sub> <sup>2-</sup>	(mg/l)	20.00	350.00	5.00	745.00
F <sup>-</sup>	(mg/l)	0.00	0.00	1.00	0.00
Total Alkalinity	(mg/l HCO <sub>3</sub> )	480.00	200.00	281.00	1,155.00
Carboxylic acids	(mg/l HAc)	0.00	0.00	28.00	0.00
TDS (measured)	(mg/l)	68,050	303,160	70,900	85,121
Calc. Density (STP)	(g/ml)	1.044	1.194	1.045	1.054
CO <sub>2</sub> Gas (STP)	(%)	2.29	0.20	0.27	6.99
H <sub>2</sub> S Gas (STP)	(%)	0.00	0.00	0.01	2.26
Total H <sub>2</sub> Saq (STP)	(mgH <sub>2</sub> S/l)	0.00	0.00	4.32	197.79
pH, measured at STP	pH	6.86	7.65	7.58	6.81
Use pH measured at STP to calculate SI?	1-Yes;0-No	0	0	0	0
Gas/Day	(10 <sup>3</sup> SCF)	12,000	0	8,500	15,100
Oil/Day	(STB)	105	0	1,000	30,046
Water/Day	(STB)	100	100	100	5,000
B-H Temp	(°F)	289	77	340	132
W-H Temp	(°F)	40	40	40	40
B-H Pres	(psia)	9,762	7000	7,000	3,330
W-H Pres	(psia)	5,000	15	15	20
Use 30Oil & 0.6gas to calc. P b.pt.?	1-Yes;0-No	0	0	0	0
If No, then Oil grav.	API grav.	40.00	40.00	40.00	40.00
and Gas Sp.Grav.:	Sp.Grav.	0.81	0.81	0.81	0.81
MeOH/Day (0%)	(STB)	0	0	0	0
MeOH/Day (10%)	(STB)	11.1	11.1	11.1	555
MeOH/Day (20%)	(STB)	25	25	25	1250
MeOH/Day (30%)	(STB)	42.85	42.85	42.85	2142.5
MeOH/Day (40%)	(STB)	66.67	66.67	66.67	3333.5

<sup>1</sup> Typical Input screen from ScaleSoftPitzer V.4.0.

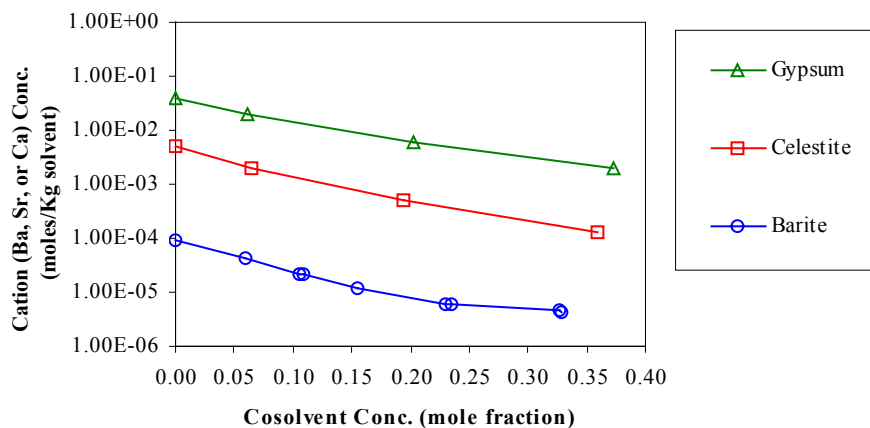


Figure 1. Plot of Ba, Sr, and Ca concentrations versus methanol concentrations measured in the dissolution experiments where barite, celestite and gypsum solids were dissolved in methanol-NaCl (1 m)-H<sub>2</sub>O solutions at 25 °C.

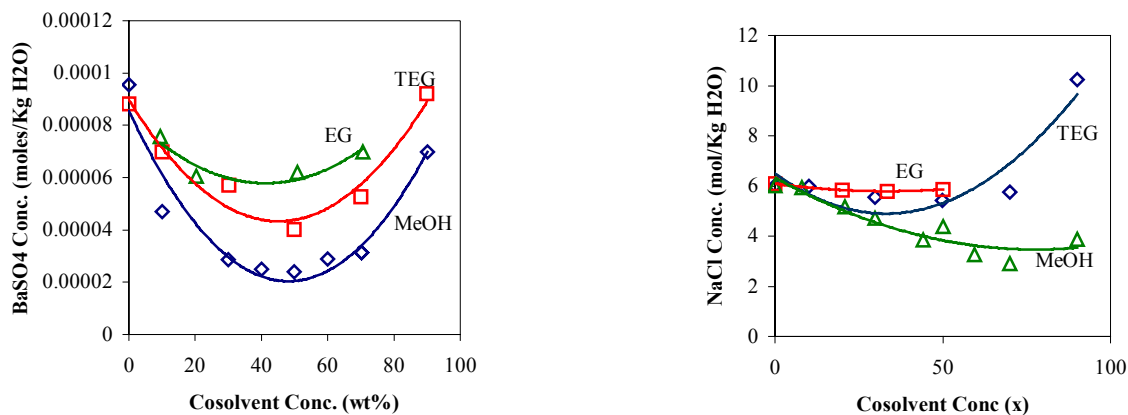


Figure 2. Plot of the barium sulfate and sodium chloride solubilities versus cosolvent concentrations, where three hydrate inhibitors (methanol, ethylene glycol, and triethylene glycol) are compared.

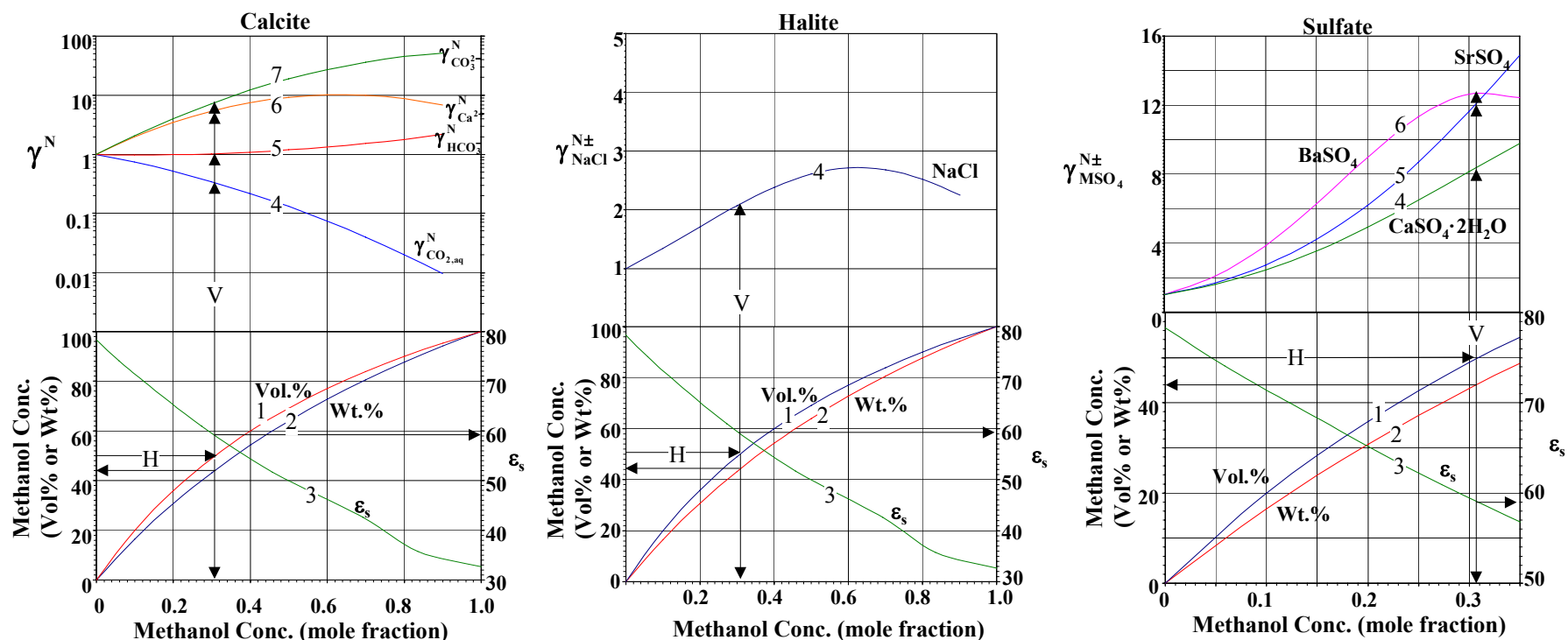
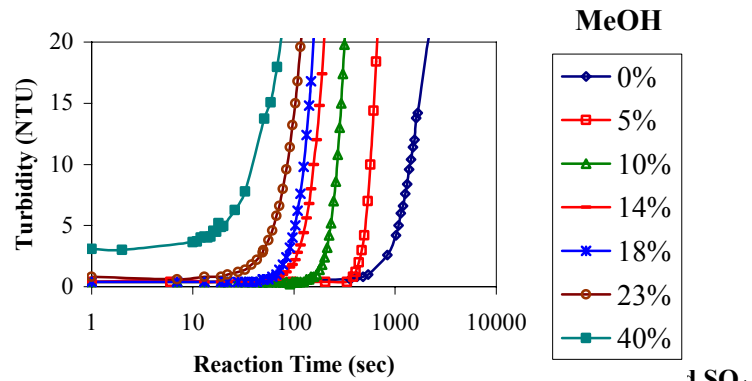


Figure 3. Nomograms to determine  $\gamma^N$ ,  $\gamma_{\text{MA}}^{N\pm}$  and solution dielectric constants for calcite, barite and halite from methanol vol%, wt%, or mole fraction concentrations, where  $\gamma^N$  and  $\gamma_{\text{MA}}^{N\pm}$  values are calculated from equations listed in Table 8. For illustration, arrows are drawn to show the users how to find all parameters at 50% (vol) methanol concentrations. All data is for 25 °C. For example, 50 vol % methanol = 44 wt % = 0.308 mole fraction,  $\gamma_{\text{CO}_3^{2-}}^N = 7.5$ ,  $\gamma_{\text{Ca}^{2+}}^N = 5.6$ ,  $\gamma_{\text{HCO}_3^-}^N = 1.0$ ,  $\gamma_{\text{CO}_2, \text{aq}}^N = 0.3$ ,  $\gamma_{\text{NaCl}}^{N\pm} = 2.1$ ,  $\gamma_{\text{SrSO}_4}^{N\pm} = 12.1$ ,  $\gamma_{\text{BaSO}_4}^{N\pm} = 12.7$ ,  $\gamma_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}}^{N\pm} = 8.4$ , and  $\epsilon_s = 59$ .

a.



b.

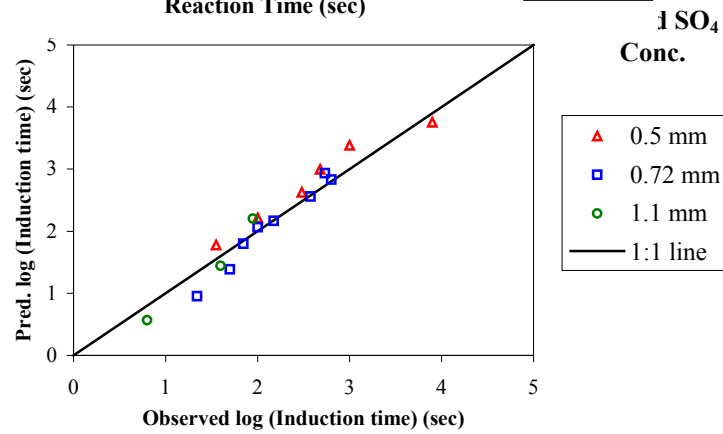
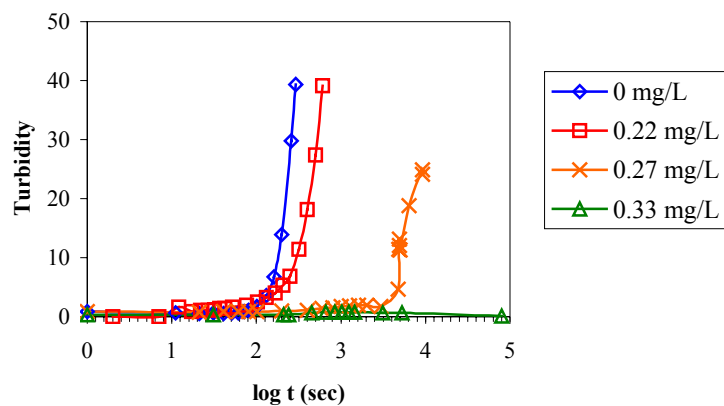
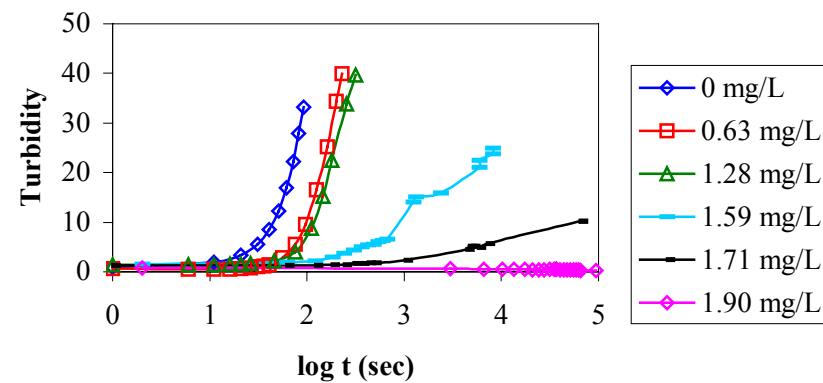


Figure 4. Plots of (a) the turbidity reading of a solution after mixing an equal volume of a cationic solution (1 m NaCl, 0.09 m Ca, and 1.50 mm Ba) and an anionic solution (1 m NaCl, 0.09 m Ca, and 1.44 mm SO<sub>4</sub>) at 25 °C versus time (sec). The final Ba and SO<sub>4</sub> concentrations are 0.75 and 0.72 mm, which correspond to  $SI_{\text{barite}} = 1.6$  in the absence of methanol; and (b) the predicted logarithmic induction time (sec) by Eq. 11 versus observed logarithmic induction time (sec). The data were from nucleation kinetics experiments at three different Ba and SO<sub>4</sub> concentrations and 0 - 40% methanol concentrations.

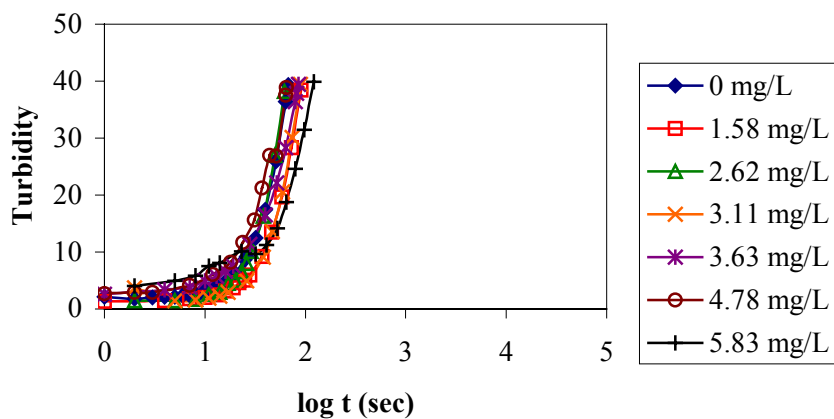
a. 0% cosolvent,



b.. 20% methanol



c.. 40% methanol



d. 40% ethylene glycol

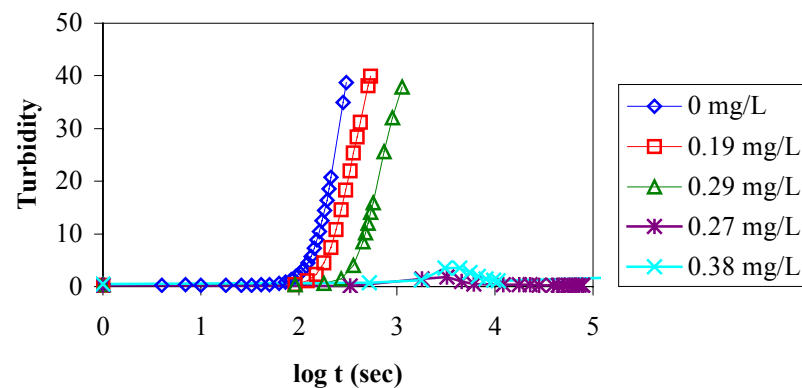
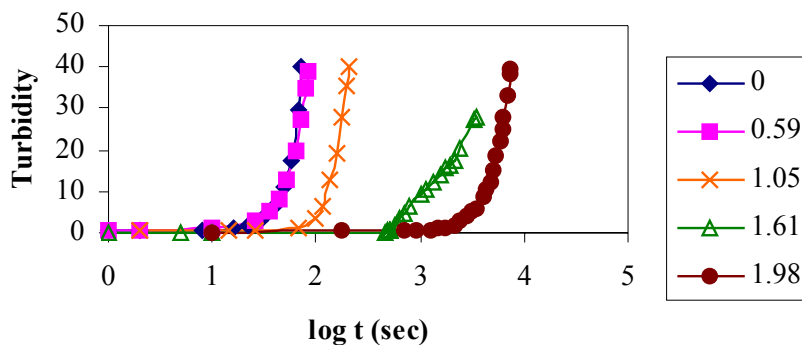
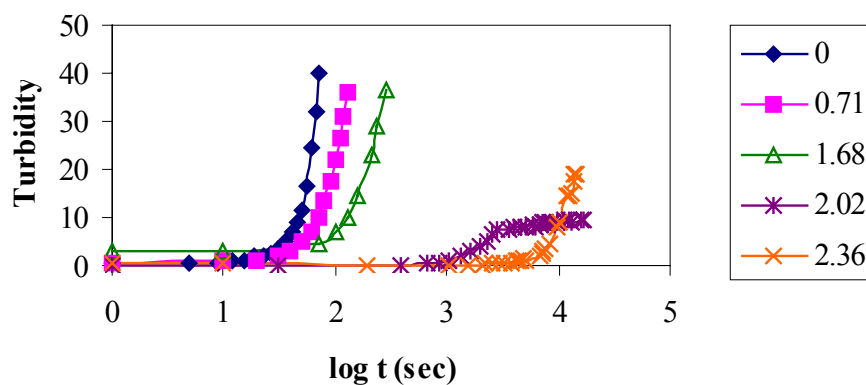


Figure 5. Plots of the turbidity reading versus time following the mixing of a barium containing solution in the presence of 0 - 40% (wt) methanol or ethylene glycol and various concentrations of BHPMP at 25 C. The mixed solution has the composition of  $[Ba] = [SO_4] = 1.1m$ ,  $[Ca] = 0.09m$ ,  $1m$  l,  $77^\circ F$  and with a PIPES buffer at pH 6.4. The solution is supersaturated with respect to  $BaSO_4$ . In the absence of methanol, the SI for barite = 2.0.

a. 0% cosolvent



b. 40% Ethylene glycol, barite



c. 40% Triethylene glycol

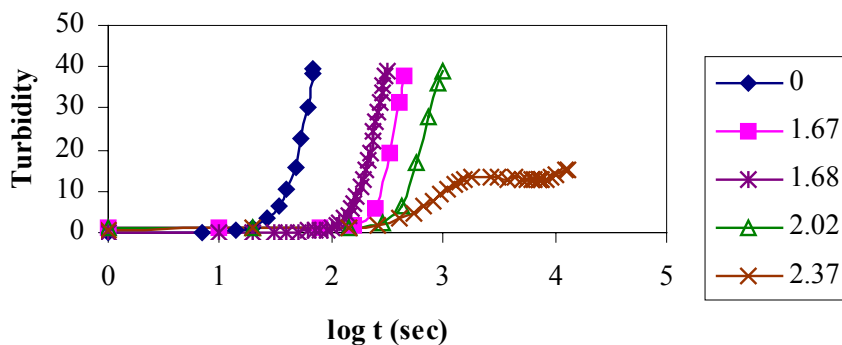


Figure 6. Plots of the turbidity reading versus time following the mixing of a barium containing solution in the presence of 0 and 40% (wt) ethylene glycol or triethylene glycol and various concentrations of BHPMP at 25 C. The mixed solution has the composition of  $[Ba] = [SO_4] = 1.8m$ ,  $[Ca] = 0.045m$ , 1 m l, 77 °F and with a PIPES buffer at pH 6.4. The solution is supersaturated with respect to  $BaSO_4$ . In the absence of methanol, the SI for barite = 2.5.

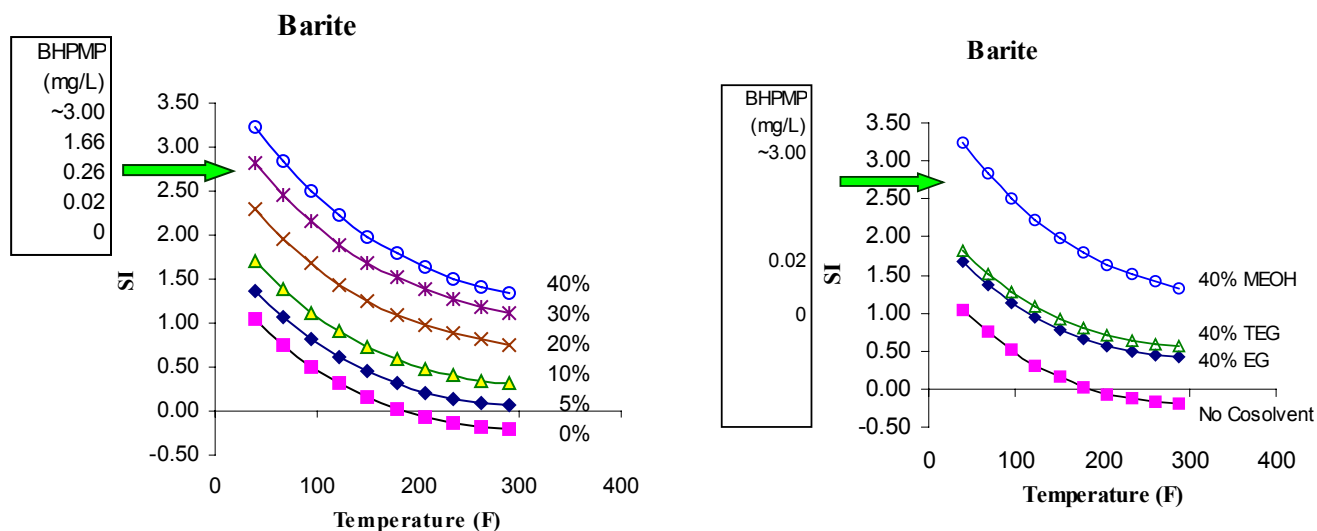


Figure 7. Plot of the ScaleSoftPitzer simulated barite saturation indices and estimated minimum BHPMP inhibitor concentration needed versus temperature to inhibit barite scale formation when 0 to 40% (by vol.) of hydrate inhibitors are mixed with the brine. The brine composition and operation condition is simulated using the data of a gulf coast well (see Table 3).

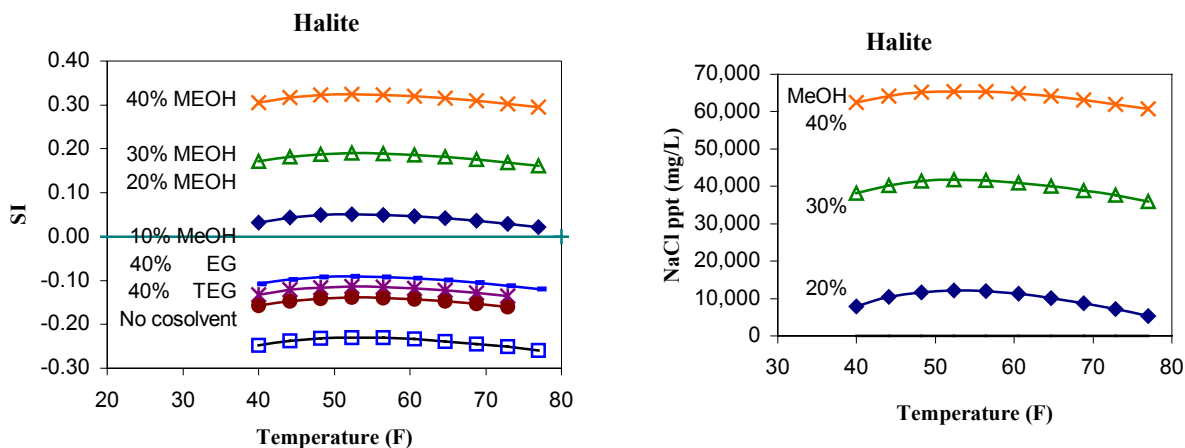


Figure 8. Plot of the ScaleSoftPitzer simulated halite saturation indices and estimated halite precipitation concentration versus temperature to inhibit barite scale formation when 0 to 40% (by vol.) of methanol, ethylene glycol and triethylene glycol is mixed with the brine. The brine composition is the formation brine composition of Smackover formation, Ar.

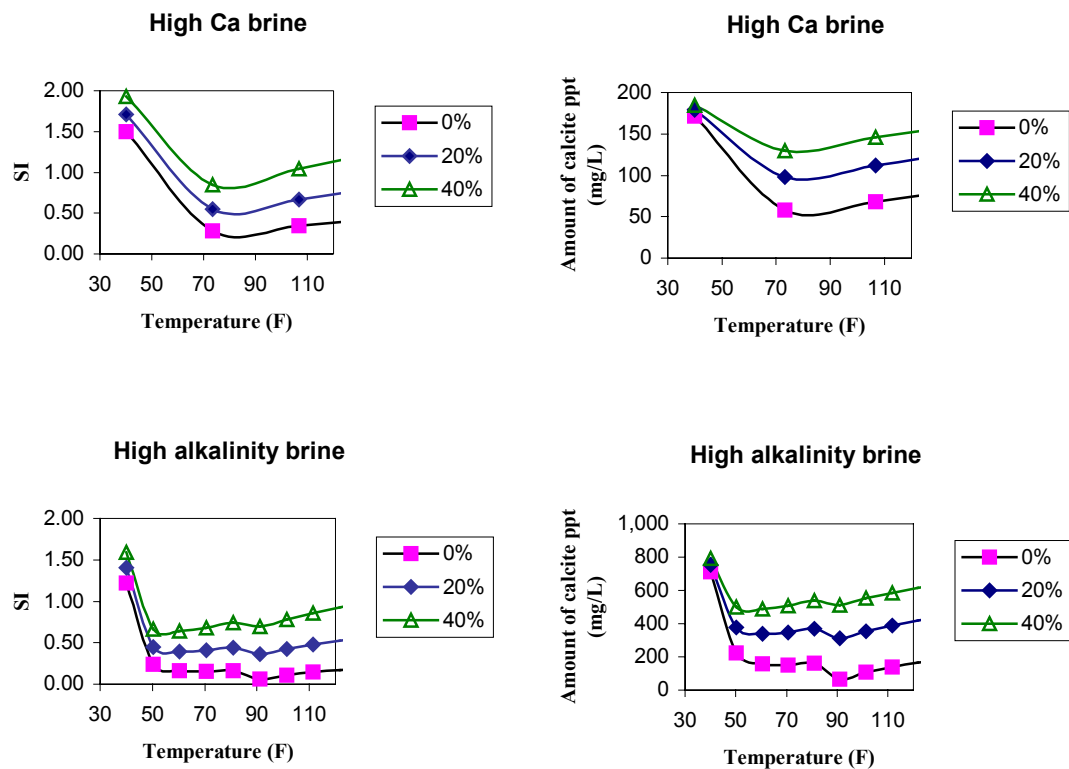


Figure 9. Plot of the ScaleSoftPitzer simulated calcite saturation indices and the amount of calcite precipitation concentration versus temperature when 0 to 40% (by vol.) of methanol is mixed with the brine. The brine composition is the formation brine compositions from two Texas wells, one contains high calcium and low  $\text{CO}_2$  and low bicarbonate and the other contain high alkalinity, high  $\text{CO}_2$ .